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Torrefaction of agriculture straws and its application on biomass pyrolysis poly-generation

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HIGHLIGHTS

- Torrefaction darkend the color and improved the grindability of agricultural straws.
- Torrefaction had different effects on char, liquid oil and biogas during pyrolysis.
- Char yield of pyrolysis torrefied straw increased and its fuel property not changed.
- Liquid oil is upgraded and concentrated phenols with less water content below 40 wt.%.
- Biogas is concentrated H_2 and CH_4 with higher LHV up to 15 MJ/nm^3.

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ABSTRACT

This study investigated the properties of corn stalk and cotton stalk after torrefaction, and the effects of torrefaction on product properties obtained under the optimal condition of biomass pyrolysis polygeneration. The color of the torrefied biomass chars darkened, and the grindability was upgraded, with finer particles formed and grinding energy consumption reduced. The moisture and oxygen content significantly decreased whereas the carbon content increased considerably. It was found that torrefaction had different effects on the char, liquid oil and biogas from biomass pyrolysis polygeneration. Compared to raw straws, the output of chars from pyrolysis of torrefied straws increased and the quality of chars as a solid fuel had no significant change, while the output of liquid oil and biogas decreased. The liquid oil contained more concentrated phenols with less water content below 40 wt.%, and the biogas contained more concentrated H_2 and CH_4 with higher LHV up to 15 MJ/nm^3.

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1. Introduction

An efficient, clean, and renewable energy source with near-zero emission of CO_2 and low pollutants emission, biomass has recently attracted increasing research attention. As an agricultural country, China generates a large amount of agricultural straw wastes annually, and over 703 million tons of straw were produced in 2007 alone (Shi, 2011), over half of which could be utilized as energy source. However, the low bulk density, high moisture content, degradation during storage, and low energy density of raw lignocellulosic biomass are critical challenges in using agricultural residues as cellulosic feedstock. Thus, the pretreatment of biomass is necessary to improve its quality for efficient energy conversion.

Torrefaction, also known as a mild-pyrolysis for the pretreatment of biomass, is a thermal process that occurs at 200–300 °C under an inert atmosphere and at low heating rates (Prins, 2005). During the torrefaction process, biomass is dried, releasing a large amount of CO (~20%) and CO_2 (~80%) and small amount of volatile organics simultaneously (Prins et al., 2006b). The volume of the original material can be reduced by 30–70%, and the material retains over 90% of the original energy in the biomass (Medic et al., 2010). Torrefaction not only upgrades the fuel properties of biomass, but also increases the grindability of biomass (Kokko et al., 2012; Ohliger et al., 2013; Van Essendelft et al., 2013). Phanphanich and Mani (2011) showed that the energy consumed in milling torrefied sawdust decreased from 237 kWh/t to 23 kWh/t. In terms of molecule mechanism, torrefaction increases the amount of atomic carbon and decreases that of atomic hydrogen and oxygen, making agricultural straws suitable for thermal conversion into energy (Medic et al., 2010; Uemura et al., 2013). Pimchuai et al. (2010) investigated the combustibility of torrefied rice husk in the spout-fluid bed combustor and found that torrefied husks ignited faster and raised the bed temperature to a higher level because of

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its low moisture content. Couhert et al. (2009) investigated the effect of torrefaction on syngas products, and observed that torrefied beech wood produced approximately the same quantities of CO_2, 7% more H_2 and 20% more CO compared with the parent wood.

Compared with products from combustion and gasification, the properties of products obtained from pyrolysis are more likely to be influenced by the chemical compositions of feedstock (van der Stelt et al., 2011). Torrefaction can affect the properties of pyrolytic products by changing the chemical composition of biomass. Meng et al. (2012) analyzed the composition of oils from fast pyrolysis of torrefied and raw loblolly pine chips and found that bio-oils from torrefied samples became more concentrated in pyrolytic lignin with less water content than that from raw samples. Zheng et al. (2013) reported that the acetic acid and furfural content of the bio-oil decreased with the increase of torrefaction temperature or residence time. And several other studies suggested that torrefaction could reduce the yield of bio-oil, carbon conversion efficiency and energy conversion efficiency of fast pyrolysis (Boateng and Mullen, 2013; Liaw et al., 2013; Zheng et al., 2012). Ren et al. (2013) investigated the microwave pyrolysis of torrefied Douglas fir sawdust pellet and found that in the pyrolysis oil from torrefied biomass the concentrations of phenols and sugars increased while the concentrations of guaiacols and furans were reduced. In addition, torrefaction also altered the compositions of syngas by reducing CO_2 and increasing H_2 and CH_4.

Despite the theoretical findings reviewed above, the utilization of bio-oil is currently limited in China because of the relatively poor economic efficiency (Hu et al., 2010), even though bio-oils from torrefied feedstocks contain concentrated phenols and sugars. In our previous works (Chen et al., 2012), the biomass-based pyrolytic polygeneration system was put forward to generate solid char, liquid oil, and biogas from biomass compared with fast pyrolysis for bio-oil alone. The polygeneration system demonstrates high potential for industrial utilization and several demonstration projects have been built and in operation in China. Because of the huge demand and the high quality of biogas and char, these demonstration projects had gained more profits than projects adopting other technologies such as gasification for biogas and combustion for electricity.

However, the high energy consumption of feedstock pretreatment, especially the grinding of biomass, and the waste of liquid oil due to the high water content, prevent further enhancement of economic efficiency of these demonstration projects. Torrefaction has the potential of reducing grinding consumption of feedstocks and improving the utilization quality of products from biomass pyrolysis. Therefore, introducing torrefaction into biomass pyrolytic polygeneration may offer a new path to enhance the economic efficiency. But little research attention is paid to investigate the influence of torrefaction on biomass pyrolytic polygeneration, especially how to optimize torrefaction conditions when it is introduced to the pyrolytic polygeneration system.

In this study, the properties of two typical Chinese agricultural straws after torrefaction (cotton stalk and corn stalk) were firstly investigated, and four torrefaction conditions in varied temperatures were discussed. The subsequent pyrolysis based on the optimum condition of biomass pyrolytic polygeneration was carried out for the raw and torrefied stalks to investigate the influence of torrefaction on the yield and composition of pyrolysis products. An optimal torrefaction condition to biomass pyrolytic torrefaction was found.

2. Methods

2.1. Materials

The agricultural straws used were cotton stalk and corn stalk, which were collected from Wuhan and Xiaogan, Hubei province, respectively. All the straws were naturally dried after being reaped. Then, the collected straws were stored in a wareroom with good ventilation.

2.2. Physico-chemical property measurement of torrefied straws

Straws were torrefied using a fixed bed to investigate the effects of torrefaction on its physico-chemical properties. Fig. 1 in Supplementary material (Fig. 1S) shows the fixed-bed torrefaction system composed of a vertical tube (I.D.: 38 mm and *H*: 600 mm), an electrical furnace, a gas condensing system, and an incondensable gas collection and analysis system. The tube was pre-heated to a preset temperature (200, 230, 260 or 290 °C). After the temperature stabilized, the sample (5 g, particle size: 2–3 cm) was quickly placed in the center of the reactor and kept for 30 min. The heating rate measured was up to 20–35 °C min^{-1} which would not influence the products (Deng et al., 2009). Pure N_2 (99.99%) was purged continuously to maintain an inert atmosphere. After pretreatment under an N_2 atmosphere, the solid products were cooled to ambient temperature in approximately 25 min and were subsequently collected for further analysis.

The grindability experiments on the raw and torrefied straws were conducted based on the previous study (Abdullah and Wu, 2009), but a cutting mill (Taiwan Chyun Tseh Industrial Co., Ltd., output of 0.75 kW) was used instead of the laboratory ball mill. To calculate the energy consumption during the grinding, the instantaneous output of the power of the mill was collected by a multi-function transducer (HarnWell, D800) connected to a computer where the time-power data was stored. The raw and torrefied samples (particle size: 2–3 cm) were placed into the cutting cell, and the cutting mill operated at a rotating speed of 2850 r/min. In each experiment, the same volume of raw or torrefied samples (approximately 30 ml) were placed in the cell to ensure consistent energy consumption for the cutting mill. The grinding duration was sufficiently long to ensure that all output particles could pass the 100 mesh sieve (<0.152 mm). The particle size distribution was measured using a British particle size analyzer (Master Min, MALVERN2000, British). Five trials were performed for each sample, and the results were averaged.

The proximate and elemental components of the torrefied straws were measured using SDTGA-2000 (Las Navas Company, Spain) and an elemental analyzer (Vario EL II CNHS/O, Germany). The higher heating value (HHV) of the raw and torrefied samples was measured using an oxygen bomb calorimeter (Parr 6300, American).

2.3. Pyrolysis and the characteristic of products

The raw and torrefied straws were pyrolyzed in the same fixed bed described in Section 2.2. In our previous works (Chen et al., 2012), the optimum temperature for obtaining high-quality pyrolytic products from the biomass polygeneration system was 550–650 °C. Therefore, the selected pyrolysis temperature of raw and torrefied biomass in the fixed bed was 550 °C. For each trial, about 3 g of sample was loaded into the sample carrier and placed on the top of the reactor before heating. A flow of preheated nitrogen (99.99%, 1 L/min) was used to provide an inert atmosphere in the reactor. When pyrolyzing the cotton stalks, the reactor was heated to the experimental temperature from the ambient temperature by the furnace at a rate of 30 °C/min. After the experimental temperature was reached, the sample carrier was moved rapidly from the top to the heated zone of the reactor. The samples were rapidly heated and decomposed, and the volatiles were purged out by N_2. Subsequently, the condensable volatiles were collected in an ice-water condenser, whereas the non-condensed parts were filtered through a glass wool filter and cleaned. The gaseous product was dried using silica gel and then collected using a gasbag and analyzed using micro gas chromatography (micro-GC). The water content of liquid oil was measured by Karl–Fischer titration (Titro-Line KF-10, SCHOTT, Germany) according to the ASTM D 1744 protocol prescribed by the American Society for Testing and Materials (titrant: Hydranal composite 2, Metrohm 787 KFTitrino). The main components of the bio-oil were determined in detail using gas chromatography–mass spectroscopy (GC–MS; HP7890 series GC with an HP5975 MS detector). The proximate and elemental composition of pyrolytic chars were also measured (Chen et al., 2012).

3. Results and discussion

3.1. Effect of torrefaction on the physic-chemical characteristics of straws

The selected samples in this work, cotton stalk and corn stalk, are typical biomass of lower energy density. The results of the proximate and ultimate analyses are listed in Table 1. Compared with fossil fuel, agricultural straw shows higher volatile and water content and contains higher proportion of oxygen and hydrogen than coal. The lower heating value also results in a lower energy density compared with that of fossil fuel. Therefore, it is necessary to apply an efficient pretreatment technology to biomass before large-scale energy utilization.

3.1.1. Morphology of torrefied stalks

Fig. 2S shows the morphology of the raw and torrefied samples. The torrefied samples was of darker brown color and subsequently blackened as the torrefaction temperature increased (from 260 °C to 290 °C) in contrast to the yellow color of the raw samples. The yellow color may result from the residue of plant pigment, including porphyrins, carotenoids, anthocyanins and betalains, which are thermally unstable (Goodwin, 1976). With the increasing severity of torrefaction, these chemicals were decomposed. On the other hand, after torrefaction carbon content increased relatively, as shown in Section 3.1.3. As a result, the color of torrefied stalks becomes darken.

3.1.2. Particle size distribution and energy consumption of grinded torrefied stalks

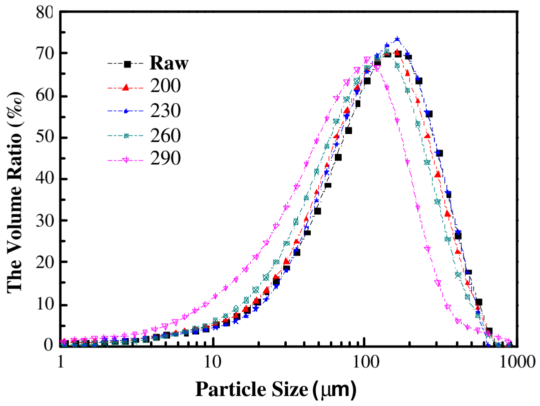
As shown in Fig. 1, the amount of ground particles (<100 μm) in the original straw samples was very small, whereas the larger particles (>140 μm) constituted about 40–60% of the samples, because the straw samples contain soft and fibrous textures that are difficult to grind. The amount of larger particles (>270 μm) of torrefied stalks at 200 °C and 230 °C increased slightly compared to raw sample according to the particle size analyzer. However, the samples torrefied at 200 °C and 230 °C take less grinding time to pass the 100 mesh sieve compared to raw samples because the larger particles are long cylindrical particles with cylinder diameter below 0.152 mm that can pass the mesh sieve. When temperatures are up to 260 °C and 290 °C, the particles of samples after torrefaction tend to be fine particles (<140 μm) because more water and some oxygen-containing compounds are released, and the degree of carbonization is exacerbated, making the particles more fragile. In terms of the torrefaction mechanism, the toughness of the straws decreased because of the changes in the micro-fiber orientation of lignin (Prins et al., 2006b), and the torrefied samples became spherical in shape with the increase of temperatures (Arias et al., 2008). These findings indicate that torrefaction can significantly improve grindability. Thus, torrefaction is an efficient approach to improving transportation of biomass through mitigating its poor mobility (Zulfiqar et al., 2006). Based on the instantaneous power consumption curve (P-t) of the cutting mill during grinding, the area under the P-t curve was calculated by integration to obtain the specific grinding energy consumption (E_g) of raw and torrefied straws. The value of E_g included the energy consumed to grind straw particles and the energy required by the mill under no-load conditions. However, the change of E_g, as shown in Table 2, illustrates the potential energy saving during the grinding of torrefied straws in comparison to raw straws. The E_g of raw corn stalk and cotton stalk are up to 194.56 kWh/t and 228.46 kWh/t, respectively. In addition, a significant decrease of E_g is observed when the torrefied temperature increases from 200 °C to 290 °C, a result that is consistent with other studies (Kokko et al., 2012; Phanphanich and Mani, 2011; Repellin et al., 2010).

Table 1
Proximate and ultimate analysis of raw stalks.

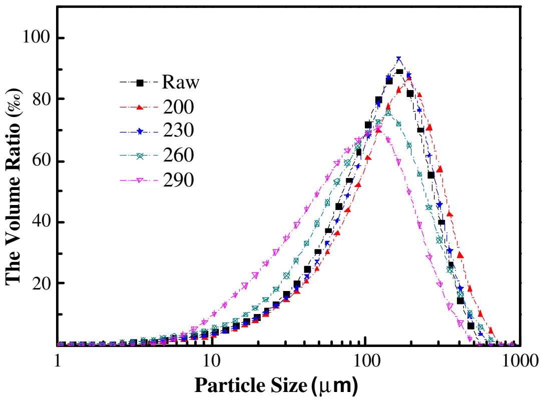
	Cotton stalk	Corn stalk
Ultimate analysis (d, wt.%)		
C	47.43	44.94
H	6.65	6.54
N	1.21	1.28
S	0.36	0.34
O[a]	39.54	38.22
Proximate analysis (ad, wt.%)		
Moisture	4.66	5.02
Volatile	74.96	70.17
Ash	4.59	8.25
Fixed caron	15.8	16.56
LHV (MJ/kg)	18.31	18.06

ad: air dry basis; d: dry basis.

[a] By difference.



(a) cotton stalk



(b) corn stalk

Fig. 1. Particle size distribution of raw and torrefied straws.

The values of E_g for torrefied straws obtained at 260–290 °C are close in value, and compared to raw straws, torrefaction at 260 °C have reduced grinding energy consumption by 5 times for cotton stalk and by 6 times for corn stalk. This can reduce the operating costs of the biomass pyrolysis polygeneration as well as the mass loss of feedstock.

3.1.3. Fuel properties of torrefied stalks

The results of the proximate and ultimate analyses on torrefied straws are listed in Table 3. The volatile matter of both samples changed minimally at temperatures of 200–230 °C, whereas noticeable reduction was observed at torrefaction temperatures of 260–290 °C. Moreover, similar observations were made in the previous studies on torrefied wood briquette and other biomass species (Felfli et al., 1999; Lipinsky et al., 2002; Prins et al., 2006a). An increase in the ash content of torrefied biomass was observed because of the mass loss (concentration effect) during the torrefaction reaction. The mass loss is primarily due to the drying of water and the release of some light volatile matter, resulting in the release of a large amount of water and some CO_2, CO, etc. Furthermore, light hydrocarbon was formed and released. Consequently, the oxygen content decreased considerably, and the elemental carbon fraction increased significantly. The decrease of hydrogen and oxygen content of the torrefied biomass suggests that the content of hydroxyl groups is reduced during torrefaction. As shown in Table 3, the HHV of torrefied straw increased significantly with the increase of torrefaction temperatures because of the increase of relative concentration of C—C and C—H bond after the removal of C—O bond during torrefaction. The relative increase in carbon content improves the combustion characteristics as the low values of O/C and H/C ratios reduce thermodynamic losses (over-oxidation), smoke, and water vapor and increases the calorific value (Bergman et al., 2005).

3.2. Effect of torrefaction on the product property from biomass pyrolysis poly-generation

3.2.1. The yield distribution of torrefied stalks

Fig. 2 shows the yield distribution of products for raw and torrefied straws vs the torrefaction temperature under the optimal condition of biomass poly-generation. For both straws, with the increase of torrefaction temperature, the yield of solid char increases while the yield of liquid oil and biogas decreases. Compared to raw straws, torrefaction at 290 °C increases the yield of solid char by 2 times and reduces the yield of liquid oil by half for both straws. The significant change of pyrolytic product yield may be primarily due to the change of chemical composition shown in Table 3, especially, the significant reduction of oxygen content which could reduce the formation reactivity of volatiles and the crosslinking reaction during torrefaction (Zheng et al., 2013). The significant increase of solid char after torrefaction at 290 °C can increase the economic value of the biomass pyrolysis poly-generation. As shown in Fig. 3, the increase of solid char yield based on dry biomass further confirmed that torrefaction can increase the solid char yield of biomass pyrolysis polygeneration. However, the more significant decrease of biogas and liquid oil yields are observed. The decreasing in biogas yield based on the feedstock of biomass pyrolysis polygeneration means more feedstock is needed to meet the production target of biogas. In addition, the waste of liquid oil may be reduced due to the decrease of liquid oil yield. The result is consistent with several previous works on the fast pyrolysis of torrefied biomass(Boateng and Mullen, 2013; Liaw et al., 2013; Meng et al., 2012; Ren et al., 2013; Zheng et al., 2012, 2013). In summary, introducing torrefaction into biomass pyrolysis polygeneration increases the output of solid char and decreases the output of liquid oil, while the output of biogas remains unchanged.

3.2.2. The composition distribution of biogas from torrefied stalks

Fig. 4 shows the composition distribution of biogas products for raw and torrefied straws vs the torrefaction temperature. In the biogas products from the raw straws, the content of CO_2 is up to 48% and 42% for cotton stalk and corn stalk, respectively. After torrefaction, a decreasing trend of the content of CO_2 in biogas is observed. Increasing the torrefaction temperature from 200 °C to 290 °C, the content of CO_2 is reduced from 47% to 35% for cotton stalk and from 40% to 25% for corn stalk. In contrast to the change of CO_2, an increasing trend is observed in the changes of the content of H_2 and CH_4 for both straws. For the torrefied straws obtained at 290 °C, the content of H_2 in the biogas is up to 14–22% for cotton stalk and corn stalk, respectively. Compared to the raw straws, the rate of increase is up to 77–135% for cotton stalk and corn stalk, respectively. However, the rate of increase for CH_4 is lower than that for H_2 and is up to 24% and 44% for cotton stalk and corn stalk, respectively. Meanwhile, the rates of decrease for CO_2 are 28–38% for cotton stalk and corn stalk, respectively, which are close to the rate of increase for CH_4. Different from H_2, CH_4 and CO_2, the content of CO generated from variable torrefied straws has no significant change. In fact, as shown in Fig. 3, the yield of gas product based on the received biomass after the torrefaction and pyrolysis process, has decreased largely compared with the raw samples. Furthermore, to explain the change of different composition in biogas, the accumulated amount of each composition released is shown in Fig. 3S. Although the rate of increase of H_2 content in biogas is the highest, the released absolute amount of H_2 based on received biomass has no obvious change, and is about 1 mmol/g dry biomass. It is suggested that torrefaction has no obvious effect on the release of H_2. However, the absolute amount of CH_4, CO, and CO_2 released has obviously decreased after torrefaction. The amounts of CO_2 released from raw stalks are up to 4.81–4.28 mmol/g for cotton stalk and corn stalk, respectively. After torrefaction at 290 °C, the amount of CO_2 released is reduced to 1.49–1.01 mmol/g, decreased by 76% and 69% compared with that of raw stalks, for cotton stalk and corn stalk, respectively. The reduced release of CO_2 may be caused by the degradation of hemicellulose and cellulose during torrefaction (Chen and Kuo, 2011) because CO_2 was resulted from the decarboxylation of hemicellulose and cellulose at lower temperature (Chen et al., 2012). The rate of decrease of CO is lower than that of CO_2 although the released amount of CO is always lower than that of CO_2. Decarbonylation process was considered as the major formation reaction of CO (Chen et al., 2012; Yang et al., 2006). During torrefaction, some new carbonyl groups would be generated (Zheng et al., 2012, 2013) and these new carbonyl groups may release CO during the subsequent pyrolysis. Therefore, the rate of decreasing of CO is

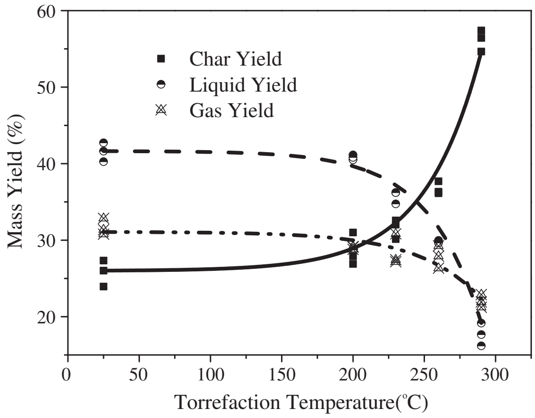
Table 2
The specific energy consumption when grinding biomass from 2 to 3 mm to 0.152 mm (kWh/t).

	Raw	200	230	260	290
Cotton stalk	194.56 (8.46[a])	122.47 (6.84)	72.34 (6.21)	31.52 (3.48)	27.47 (6.48)
Corn stalk	228.46 (10.87)	154.87 (9.78)	105.78 (12.63)	46.89 (6.67)	35.49 (6.24)

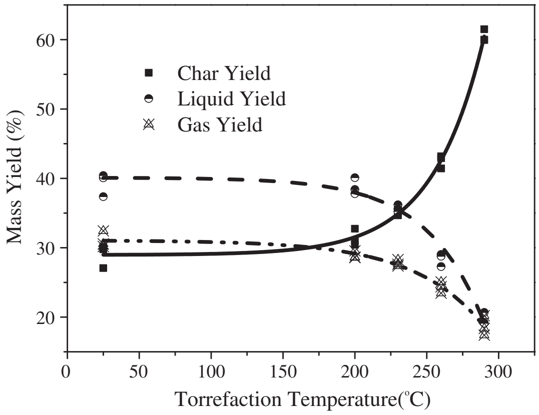
[a] Number enclosed in the parenthesis were standard deviations with $n = 3$.

Table 3
The proximate and ultimate analysis of torrefied straw.

Sample	Proximate analysis(ad)				Ultimate analysis (d)				HHV (MJ/kg)
	M	V	A	FC	C	H	O	N	
Cotton stalk									
Raw	4.66	74.96	4.59	15.80	47.43	6.65	39.54	1.21	18.31
200	3.29	75.44	4.79	16.48	50.33	6.39	37.56	0.64	18.68
230	3.14	73.12	5.35	18.39	52.43	5.68	35.58	0.66	19.49
260	2.80	68.99	6.35	21.86	57.87	5.23	29.44	0.81	21.99
290	2.50	53.62	9.88	34.01	67.38	4.51	16.74	1.07	25.43
Corn stalk									
Raw	5.02	70.17	8.25	16.56	44.94	6.54	38.22	1.28	18.06
200	3.09	69.32	9.18	18.41	48.16	5.43	35.76	1.01	18.26
230	3.05	64.77	10.70	21.47	51.23	4.99	31.48	1.10	19.19
260	3.04	54.53	14.11	28.32	55.10	4.71	24.29	1.19	20.73
290	3.00	35.30	20.52	41.19	61.85	4.01	11.32	1.50	23.61

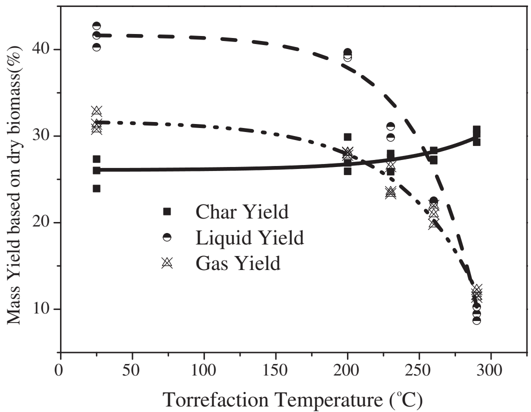


(a) cotton stalk

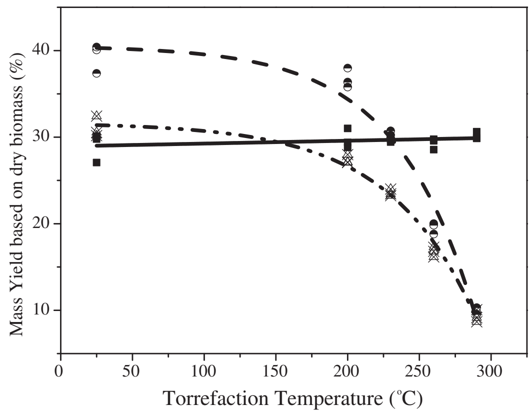


(b) corn stalk

Fig. 2. The yield distribution of products under the optimal condition of biomass poly-generation for raw and torrefied straws.



(a) cotton stalk



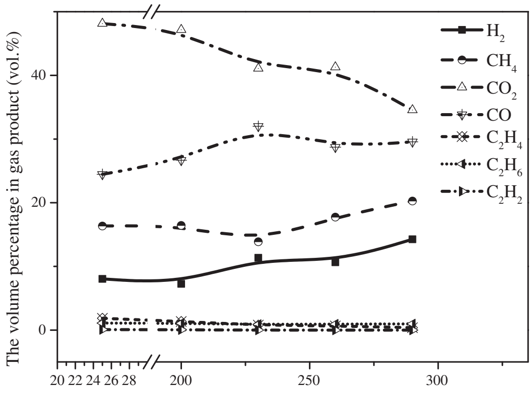
(b) corn stalk

Fig. 3. The yield distribution of products under the optimal condition of biomass poly-generation for raw and torrefied straws based on dry biomass.

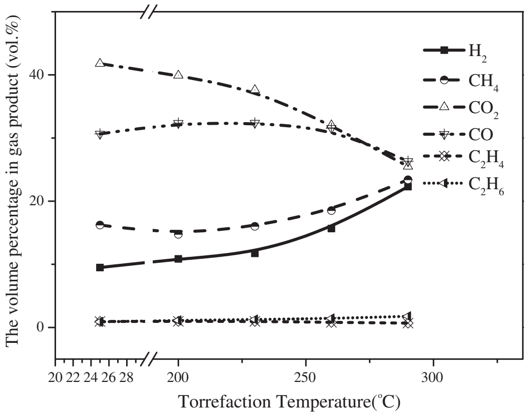
not similar with that of CO_2. Generally, CH_4 is derived from the demethoxylation during degradation of lignin (Yang et al., 2006). Compared to cellulose and hemicellulose, the degradation of lignin is not obvious (Chen and Kuo, 2011) which means that the released amount of CH_4 at subsequent pyrolysis for torrefied stalks should be similar with that of raw stalks. However, as shown in Fig. 3S, when torrefaction severity increasing, the released amount of CH_4 is reduced from 1.63 mmol/g to 0.87 mmol/g for cotton stalk and from 1.66 mmol/g to 0.92 mmol/g for corn stalk, respectively. The results suggest that torrefaction affects the structure of lignin and inhibits the dimethoxylation reaction at the subsequent pyrolysis. And, during torrefaction, the branched structure of lignin may be cross-linked to each other and these methoxy groups may be transformed to the precursor of aromatic ring (Zheng et al., 2013). Because of the obvious decrease of CO_2 as non-combustible composition and the obvious increase of H_2 and CH_4 as good combustible composition, torrefaction significantly upgrades the heat value of biogas from 11.66 MJ/m^3 to 13.40 MJ/m^3 and from 11.86 MJ/m^3 to 15.70 MJ/m^3 (as shown in Table 4) for cotton stalk and corn stalk, respectively.

3.2.3. The properties of liquid oil from torrefied stalks

Table 5 shows the water content of liquid-oil quantified by the Karl–Fischer titration and its organic composition by GC/MS. After



(a) cotton stalk



(b) corn stalk

Fig. 4. The composition distribution of gas product under the optimal condition of biomass poly-generation for raw and torrefied straws.

Table 4
The low heat value (N_2-free and H_2O-free) of gas product under the optimal condition of biomass poly-generation for raw and torrefied straws (MJ/N m^3).

	Raw	200	230	260	290
Cotton stalk	11.66	11.55	11.29	12.13	13.40
Corn stalk	11.86	11.87	12.50	13.73	15.70

torrefaction, the water content in liquid oil pyrolyzed under the optimal condition of biomass pyrolysis polygeneration has decreased significantly. Compared to raw straws, the water content obtained from the torrefied straws at 290 °C is reduced from 70.2 wt.% to 40.1 wt.% for cotton stalk and from 74.3 wt.% to 35.9 wt.% for corn stalk, respectively. This may be due to the dehydrating effect of torrefaction and the reduced generation of water in the subsequent pyrolysis. A high content of water for liquid oil generated by biomass pyrolysis polygeneration becomes the bottleneck for further improving the economic value of this technology. Therefore, by reducing the water content of liquid oil, torrefaction on biomass before the pyrolysis provides a new path to improve biomass pyrolysis polygeneration. In addition to reduce the water content, torrefaction also can influence the organic composition of the liquid oil. At first, a significant decrease of the acid content is observed (shown in Table 5), which means the pH value of liquid oil could be increased (Meng et al., 2012). The content of phenols increases with the increase of the torrefaction temperature until it reaches the maximum at 260 °C. When the temperature further increases, the phenol content slightly decreases again. The increase of phenol content in this liquid oil from torrefied biomass may be due to the relative increase of lignin in torrefied biomass. However, the fact that torrefaction at 290 °C reduces the content of phenols compared with other torrefied straw suggests that torrefaction can prevent the breaking of monomer in lignin and retain more benzene rings to participate in the char formation during pyrolysis leading to the significant increase of char yield (shown in Fig. 2). No significant change of the content of furan, ketones and cyclopentens is observed from the degradation of hemicellulose and cellulose. The mass loss of hemicellulose and cellulose during torrefaction should produce less furan, ketones and cyclopentens in the subsequent pyrolysis. However, since the rate of decreasing for acid content is higher than that for other organics, the relative content of these organics have no obvious change.

3.2.4. The properties of char from torrefied stalks

The properties of the solid chars obtained from raw and torrefied straws are listed in Table 6. Taking into account the measurement errors and sample differences, the chars from torrefied straw have no significant difference in basic properties compared with the char from raw straws. It indicated that torrefaction had no obvious impact on the basic properties when these chars are used as a solid fuel. However, torrefaction has changed the chemical composition and the internal structure of straws and influenced

Table 5
Composition of liquid-oil under the optimal condition of biomass poly-generation for raw and torrefied straws.

Samples	Water[a] (wt.% of oil)	Acid[b]	Furan[b]	Ketones[b]	Cyclopentens[b]	Phenols[b]
		(Area% of result from GCMS)				
Cotton stalk						
Raw	70.2 (10.8[c])	46.8	7.0	12.9	4.9	15.2
200	67.8 (12.2)	36.4	7.0	9.4	5.2	17.0
230	57.9 (9.1)	36.6	2.6	13.6	5.3	23.3
260	52.6 (8.4)	27.9	5.0	12.0	3.2	30.7
290	40.1 (6.7)	13.0	2.1	10.1	3.6	20.5
Corn stalk						
Raw	74.3 (11.6)	38.7	7.7	15.3	5.0	17.5
200	70.6 (10.3)	37.5	5.6	9.0	3.2	29.0
230	56.7 (11.2)	38.1	5.2	12.9	5.3	32.8
260	45.4 (9.6)	21.8	7.3	5.4	9.1	41.6
290	35.9 (8.8)	12.4	6.2	10.8	2.4	30.1

[a] The percentage value is calculated based on the total mass of liquid oil.
[b] The percentage value is calculated based on the analysis of organic components in liquid oil by GCMS.
[c] Number enclosed in the parenthesis were standard deviations with $n = 3$.

Table 6
The basic analysis of chars from raw and torrefied straws.

	Proximate analysis (ad, wt.%)				Ultimate analysis (d, wt.%)				LHV (MJ/kg)
	M	V	A	FC	C	H	O	N	
Cotton stalk									
Raw	3.12	33.77	12.70	50.41	74.63	2.18	9.46	1.30	27.46
200	2.30	30.87	15.49	51.34	74.10	2.34	6.55	1.52	26.82
230	2.75	38.78	14.13	44.34	74.84	2.27	7.44	1.32	27.32
260	2.86	30.67	11.52	54.95	76.42	2.32	8.46	1.28	28.24
290	2.41	33.08	12.64	51.87	75.20	2.34	8.60	1.22	28.04
Corn stalk									
Raw	2.57	36.12	22.41	38.90	68.42	2.02	6.01	1.14	23.51
200	3.51	35.23	21.89	39.37	69.25	1.95	5.28	1.63	24.32
230	2.89	37.06	21.67	38.38	67.12	1.89	7.89	1.43	23.06
260	2.65	34.51	22.08	40.76	65.21	2.34	8.45	1.92	24.82
290	2.49	35.77	22.41	39.33	66.36	2.16	7.54	1.53	24.11

the degradation process during pyrolysis, resulting in the significant difference in the properties of biogas and liquid oil. Therefore, the internal structure of chars from torrefied straws may be different from that of raw straw. A further investigation on the change of internal structure of chars from torrefied biomass is needed when the torrified chars are used for purposes other than combustion, e.g. activated carbon.

4. Conclusion

It is found that torrefaction with rapid temperature elevation has obvious influence on stalks, including darkened color, improved grindability, increased carbon content and decreased oxygen content. It would improve the economic efficiency to introduce torrefaction into biomass pyrolytic polygeneration because torrefaction can reduce grinding energy consumption, increase char yield but decrease liquid oil yield and the water content. However, the deceased yield of biogas suggests that a higher production scale should be designed to meet the demand of biogas. Torrefaction at 260–290 °C is suggested as the optimum condition for biomass pyrolytic polygeneration.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2013.12.088.

References

Abdullah, H., Wu, H.W., 2009. Biochar as a fuel: 1. Properties and grindability of biochars produced from the pyrolysis of mallee wood under slow-heating conditions. Energy Fuels 23, 4174–4181.

Arias, B., Pevida, C., Fermoso, J., Plaza, M.G., Rubiera, F., Pis, J.J., 2008. Influence of torrefaction on the grindability and reactivity of woody biomass. Fuel Process. Technol. 89, 169–175.

Bergman, P.C.A., Boersma, A.R., Zwart, R.W.R., Kiel, J.H.A., 2005. Torrefaction for Biomass Co-firing in Existing Coal-Fired Power Stations, BIOCOAL. Energy Research Center of the Netherlands (ECN), The Netherlands.

Boateng, A.A., Mullen, C.A., 2013. Fast pyrolysis of biomass thermally pretreated by torrefaction. J. Anal. Appl. Pyrolysis 100, 95–102.

Chen, W.H., Kuo, P.C., 2011. Torrefaction and co-torrefaction characterization of hemicellulose, cellulose and lignin as well as torrefaction of some basic constituents in biomass. Energy 36, 803–811.

Chen, Y.Q., Yang, H.P., Wang, X.H., Zhang, S.H., Chen, H.P., 2012. Biomass-based pyrolytic polygeneration system on cotton stalk pyrolysis: influence of temperature. Bioresour. Technol. 107, 411–418.

Couhert, C., Salvador, S., Commandre, J.M., 2009. Impact of torrefaction on syngas production from wood. Fuel 88, 2286–2290.

Deng, J., Wang, G.J., Kuang, J.H., Zhang, Y.L., Luo, Y.H., 2009. Pretreatment of agricultural residues for co-gasification via torrefaction. J. Anal. Appl. Pyrolysis 86, 331–337.

Felfli, F.F., Luengo, C.A., Beaton, P., Suarez, J.A., 1999. Efficiency Test for Bench Unit Torrefaction and Characterization of Torrefied Biomass, ed. Pergamon-Elsevier Science Ltd, Kidlington.

Goodwin, T.W., 1976. Chemistry and Biochemistry of Plant Pigments, Academic Press, London and New York.

Hu, X.J., Chang, S.Y., Li, J.J., Qin, Y.N., 2010. Energy for sustainable road transportation in China: challenges, initiatives and policy implications. Energy 35, 4289–4301.

Kokko, L., Tolvanen, H., Hamalainen, K., Raiko, R., 2012. Comparing the energy required for fine grinding torrefied and fast heat treated pine. Biomass Bioenergy 42, 219–223.

Liaw, S.S., Zhou, S., Wu, H.W., Garcia-Perez, M., 2013. Effect of pretreatment temperature on the yield and properties of bio-oils obtained from the auger pyrolysis of Douglas fir wood. Fuel 103, 672–682.

Lipinsky, E.S., Arcate, J.R., Reed, T.B., 2002. Enhanced wood fuels via torrefaction. Abstr. Pap. Am. Chem. Soc. 223, U587-U587.

Medic, D., Darr, M., Potter, B., Shah, A. 2010. Effect of Torrefaction Process Parameters on Biomass Feedstock Upgrading. In: ASABE Annual International Meeting, Pittsburgh, Pennsylvania. (Paper Number: 1009316.)

Meng, J.J., Park, J., Tilotta, D., Park, S., 2012. The effect of torrefaction on the chemistry of fast-pyrolysis bio-oil. Bioresour. Technol. 111, 439–446.

Ohliger, A., Forster, M., Kneer, R., 2013. Torrefaction of beechwood: a parametric study including heat of reaction and grindability. Fuel 104, 607–613.

Phanphanich, M., Mani, S., 2011. Impact of torrefaction on the grindability and fuel characteristics of forest biomass. Bioresour. Technol. 102, 1246–1253.

Pimchuai, A., Dutta, A., Basu, P., 2010. Torrefaction of agriculture residue to enhance combustible properties. Energy Fuels 24, 4638–4645.

Prins, M. 2005. Thermodynamic analysis of biomass gasification and torrefaction (Ph.D thesis). Eindhoven Technical University, The Netherlands.

Prins, M.J., Ptasinski, K.J., Janssen, F., 2006a. Torrefaction of wood – Part 1. Weight loss kinetics. J. Anal. Appl. Pyrolysis 77, 28–34.

Prins, M.J., Ptasinski, K.J., Janssen, F.J.J.G., 2006b. More efficient biomass gasification via torrefaction. Energy 31, 3458–3470.

Ren, S.J., Lei, H.W., Wang, L., Bu, Q., Chen, S.L., Wu, J., Julson, J., Ruan, R., 2013. The effects of torrefaction on compositions of bio-oil and syngas from biomass pyrolysis by microwave heating. Bioresour. Technol. 135, 659–664.

Repellin, V., Govin, A., Rolland, M., Guyonnet, R., 2010. Energy requirement for fine grinding of torrefied wood. Biomass Bioenergy 34, 923–930.

Shi, Y., 2011. China's resources of biomass feedstock. Eng. Sci. 13, 16–23.

Uemura, Y., Omar, W., Othman, N.A., Yusup, S., Tsutsui, T., 2013. Torrefaction of oil palm EFB in the presence of oxygen. Fuel 103, 156–160.

van der Stelt, M.J.C., Gerhauser, H., Kiel, J.H.A., Ptasinski, K.J., 2011. Biomass upgrading by torrefaction for the production of biofuels: a review. Biomass Bioenergy 35, 3748–3762.

Van Essendelft, D.T., Zhou, X., Kang, B.S.J., 2013. Grindability determination of torrefied biomass materials using the hybrid work index. Fuel 105, 103–111.

Yang, H.P., Yan, R., Chen, H.P., Zheng, C.G., Lee, D.H., Liang, D.T., 2006. In-depth investigation of biomass pyrolysis based on three major components: hemicellulose, cellulose and lignin. Energy Fuels 20, 388–393.

Zheng, A.Q., Zhao, Z.L., Chang, S., Huang, Z., He, F., Li, H.B., 2012. Effect of torrefaction temperature on product distribution from two-staged pyrolysis of biomass. Energy Fuels 26, 2968–2974.

Zheng, A.Q., Zhao, Z.L., Chang, S., Huang, Z., Wang, X.B., He, F., Li, H.B., 2013. Effect of torrefaction on structure and fast pyrolysis behavior of corncobs. Bioresour. Technol. 128, 370–377.

Zulfiqar, M., Moghtaderi, B., Wall, T.F., 2006. Flow properties of biomass and coal blends. Fuel Process. Technol. 87, 281–288.